Lecture 13: Physics 212

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1 Reading

1. Sections 4.3.2, 4.1 and 4.2 of Griffiths.
2. Sections 11-1, 11-2 and Chapter 12 of French and Taylor.

2 Thought Questions

1. We keep talking about *the* angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ where the momentum operator is given by $\mathbf{p} = (\hbar/i)\nabla$. But classically, the value of the angular momentum $\sum_i \mathbf{x}_i \times \mathbf{p}_i$ of some group of particles depends on the axis with respect to which various distances $\mathbf{x}_i$ are measured. In both classical and quantum mechanics, when do we have to worry about the axis which defines the positions $\mathbf{x}$?

2. Why is it obvious that

$$(L_x + iL_y)Y_l^l(\theta,\phi) = 0, \qquad (L_x - iL_y)Y_l^{-l}(\theta,\phi) = 0? \tag{1}$$

3. A particle of mass M is constrained to move on the surface of a sphere of radius R but is otherwise free. What are the energies and wave functions for this particle? Classically, the motion of such a particle would lie in a plane (why?!). Show that this classical behavior is recovered for large quantum numbers l and states of maximum z-component L_z.

4. Explain how one can use spectroscopy and the eigenvalues of the magnitude-squared angular momentum operator L^2 to determine the distance r_0 between two atoms of a diatomic molecule AB. This is a neat example of how an incredibly small distance can be "measured" by indirect means. Knowing bond lengths for different diatomic molecules is valuable information for understanding the properties of chemical bonds.

5. As we will see, the energy levels of a hydrogen atom are degenerate. Explain qualitatively why applying a uniform external electric field $\mathbf{E}$ to a hydrogen atom will decrease the degeneracy of most hydrogen levels and also discuss qualitatively whether the degeneracy will be completely lifted (no degeneracy remains). Note: a constant homogeneous external electric field $\mathbf{E} = -eE\hat{\mathbf{z}} = -\nabla V$ corresponds to a potential $V(x) = eEz$.

6. The nucleus of a hydrogen atom is not a point particle but has a finite radius of order 10^{-13} cm. Would you expect the energy levels E_n of the hydrogen atom to become slightly larger or smaller if you replaced a point nucleus with a nucleus of small but finite radius?

7. True or false and why: the solutions $u(r) = rR(r)$ of the one-dimensional radial equation for a potential $V(r)$ of spherical symmetry,

$$\frac{-\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}\right]u = Eu, \tag{2}$$

are like the solutions of the one-dimensional Schrodinger equation in that they can be chosen to be either even or odd functions.

3 Concepts to Understand

1. With a bit of elbow grease, you should be able to show that the orbital angular momentum operator $L^2 = (\mathbf{r} \times \mathbf{p})^2$ in spherical coordinates becomes the following:

$$L^2 = -\hbar^2 \left[\frac{1}{\sin(\theta)} \partial_\theta \left(\sin(\theta) \partial_\theta \bullet \right) + \frac{1}{\sin^2(\theta)} \partial_\phi^2 \right], \tag{3}$$

and we already know that in spherical or cylindrical coordinates,

$$L_z = \frac{\hbar}{i} \partial_\phi. \tag{4}$$

One can then show (see Griffiths and French/Taylor) that the simultaneous eigenfunctions of the commuting variables L^2 and L_z are the normalized *spherical harmonics*

$$Y_l^m(\theta, \phi) = \epsilon \sqrt{\frac{(2l+1)}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} e^{im\phi} P_l^m(\cos(\theta)), \tag{5}$$

which are functions defined on the surface of a unit sphere. The coefficient ϵ is defined by

$$\epsilon = \begin{cases} (-1)^m & \text{for } m \geq 0 \\ 1 & \text{for } m < 0. \end{cases}, \tag{6}$$

and the symbol $P_m^l(x)$ denotes the associated Legendre function of x and is defined by:

$$P_l^m(x) = \left(1 - x^2\right)^{|m|/2} \left(\frac{d}{dx} \right)^{|m|} P_l(x), \tag{7}$$

where the Legendre polynomial $P_l(x)$ is itself defined by a recursion relation:

$$P_0 = 1, \qquad P_1 = x, \qquad P_{l+1} = \frac{2l+1}{l+1} x P_l - \frac{l}{l+1} P_{l-1}. \tag{8}$$

The P_l are polynomials of degree l and the associated Legendre functions are polynomials in the quantities x and $\sqrt{1-x^2}$.

Note that the associated Legendre polynomials P_l^m vanish unless $|m| \leq l$ since differentiating a polynomial of order l more than l times gives zero. This is the same result that we derived earlier using ladder operators and commutation relations of angular momentum operators: for a given quantum number l indicating the magnitude squared of the angular momentum, one can have all values of magnetic quantum numbers m corresponding to $m = -l, -l+1, \cdots, l-1, l$.

The fact that the spherical harmonics are simultaneous eigenvectors of these operators then leads to the following results **which you should memorize and know**:

$$L^2 Y_l^m = l(l+1)\hbar^2 Y_l^m; \tag{9}$$

$$L_z Y_l^m = (m\hbar) Y_l^m; \tag{10}$$

$$\langle Y_l^m | Y_{l'}^{m'} \rangle = \int_0^{2\pi} \int_0^{\pi} Y_l^m(\theta, \phi)^* Y_{l'}^{m'}(\theta, \phi) \sin(\theta) \, d\theta \, d\phi \tag{11}$$

$$= \delta_{l,l'} \delta_{m,m'}. \tag{12}$$

This last result follows from our favorite theorem for Hermitian operators, that eigenvectors belonging to distinct eigenvalues are orthogonal. (Again you should remember how to prove this using ket notation!)

2. The vibration-rotational spectrum of a diatomic molecule: the energy levels of a diatomic molecule are approximately given by:

$$E_{n,l} \approx \hbar\omega_0 \left(n + \frac{1}{2}\right) + \frac{j(j+1)\hbar^2}{2\mu r_0^2}, \tag{13}$$

where ω_0 is the frequency of the parabola that interpolates near the minimum of the potential $V(r)$, $\mu = m_1 m_2/(m_1 + m_2)$ is the reduced mass of the diatomic molecule, and r_0 is distance between mass m_1 and mass m_2 of the diatomic molecules. The second rotational energy term is about 50 times smaller than the first vibrational energy term and so the rotational levels form small perturbations around the vibrational spectrum. French and Taylor on pages 487-500 gives a nice discussion of the vibrational-rotational spectrum in comparison with experimental data.

3. Eq. (3) is important for solving the three-dimensional Schrodinger equation for spherically symmetric potentials $V = V(r)$ since the kinetic energy term has a Laplacian operator ∇^2 which, in spherical coordinates, can be written:

$$\begin{aligned} \nabla^2 &= \partial_x^2 + \partial_y^2 + \partial_z^2 \qquad (14)\\ &= \frac{1}{r^2}\partial_r\left(r^2\partial_r\cdot\right) + \frac{1}{r^2\sin(\theta)}\partial_\theta\left(\sin(\theta)\partial_\theta\cdot\right) + \frac{1}{r^2\sin^2(\theta)}\partial_\phi^2 \\ &= \frac{1}{r^2}\partial_r\left(r^2\partial_r\cdot\right) - \frac{1}{\hbar^2 r^2}L^2 \\ &= \frac{1}{r}\partial_r^2(r\cdot) - \frac{1}{\hbar^2 r^2}L^2. \qquad (15) \end{aligned}$$

The angular dependence of the three-dimensional Laplacian in spherical coordinates is exactly the angular momentum operator squared!

4. Note: the spherical harmonics are quite important in many areas of applied science and mathematics. E.g., in meteorology and in oceanography, one often represents the three-dimensional time-dependent fields of velocity, pressure, temperature, etc., in terms of finite expansions of spherical harmonics (with radius-dependent coefficients) since this is a natural and economical way to approximate functions on the surface of a sphere. In particular, this approximation avoids the sometimes subtle issue of how to deal with coordinate singularities at $\theta = 0$ and $\theta = \pi$, i.e., at the north and south poles of a sphere.

   The argument goes something like this: since the Y_l^m are the eigenvectors of an observable L^2, they must form a complete set and so any function $f(\theta, \phi)$ must have an expansion in terms of them. If $w(\rho, \theta, \phi)$ denotes some field (e.g., the temperature), we can write:

$$w(\rho, \theta, \phi) = \sum_{l=0}^{\infty}\sum_{m=-l}^{l} w_{lm}(\rho) Y_l^m(\theta, \phi), \tag{16}$$

since, for any fixed radial distance ρ, we have a function of angles that can be expanded by the completeness of the Y_l^m.

By the way, this argument holds for a plane wave also. More advanced books on quantum mechanics (and many applied mathematics books) show how to expand a plane wave in terms of spherical waves:

$$e^{ikz} = e^{ikr\cos(\theta)} = \sum_{l=0}^{\infty} i^l(2l+1)j_l(kr)P_l(\cos\theta), \tag{17}$$

where $j_l(x)$ is the lth spherical Bessel function. We will possibly come back to this formula later in the course since it holds the key to understanding quantum scattering. A beam of particles along the z-axis (represented by a plane wave $\exp(ikz)$ of known momentum) impinges upon some target and stuff (particles, photons) are emitted in various directions, which can be thought of as the right side pieces of the above equation. Chapter 11 of Griffiths covers some of this material.

5. Using Eq. (15), we can show the important result that the three-dimensional single-particle Schrodinger equation for a spherically symmetric potential $V = V(r)$ reduces to solving a one-dimensional single-particle Schrodinger equation for some radial function $u(r) = rR(r)$ in a potential

$$V_{1d}(r) = V(r) + \frac{\hbar^2}{2m}\frac{l(l+1)}{r^2}, \tag{18}$$

where the full stationary three-dimensional wave function is

$$\psi(\rho, \theta, \phi) = R(r)Y_l^m(\theta, \phi), \tag{19}$$

which is simultaneously an eigenfunction of the three operators H, L^2, and L_z.

Since the spherical harmonics are already normalized, you should be able to see easily that the condition for the radial function $u = rR$ to be normalized is:

$$\int_0^\infty |u|^2 \, dr = 1. \tag{20}$$

6. The hydrogen atom is a special case of a single electron in a spherical potential, namely the Coulomb inverse-r potential $V(r) = -e^2/r$ (CGS units). The general wave function can be written:

$$\psi(r, \theta, \phi) = R(r)Y_l^m(\theta, \phi), \tag{21}$$

where the radial part of the wave function $u = rR$ satisfies the one-dimensional single-particle Schrodinger equation

$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[\frac{\hbar^2}{2m}\frac{l(l+1)}{r^2} - \frac{e^2}{r}\right]u = Eu. \tag{22}$$

Before analyzing this equation further, it is helpful to set various coefficients to one by rescaling distance and energy (units of Bohr radius $r_0 = \hbar^2/(me^2)$ and ionization energy $E_0 = me^4/(2m\hbar^2)$. We then get:

$$\partial_r^2 u + \left(\frac{2}{r} - \frac{l(l+1)}{r^2}\right)u = \epsilon u, \tag{23}$$

where we have called $\epsilon = -E/E_0$ the rescaled energy.

We can then proceed analytically just as we did for the harmonic oscillator in Physics 211, by looking for a Taylor series expansion of the solution $u(r)$, after factoring out the asymptotic behaviors in the limit $r \to 0$ and $r \to \infty$. The details are given in Griffiths and in French/Taylor. One discovers that the radial function has the form:

$$u(r) = u_{nl}(r) = r^{l+1}e^{-r}p_{n,l}(r), \tag{24}$$

of a power of r times a decaying exponential times a polynomial of order $n-l-1$ for some integer $n \geq 1$ called *the principle quantum number*, which identifies the number of nodes in the radial wave function. This corresponds to an energy level:

$$E_n = \tag{25}$$

One has the important inequality:

$$l \leq n - 1, \tag{26}$$

i.e., for a given energy level n of the hydrogen atom, the angular momentum number l (which determines the magnitude squared of $\mathbf{L}$) can not be larger than $n-1$. Thus the lowest energy state of the hydrogen atom has $n = 1$, $l = m = 0$.

7. The fact that the energy of the hydrogen atom does not depend on the orbital angular momentum number l is unique among spherically-symmetric potentials, it holds only for the Coulomb $1/r$ potentials. It is related to the fact that orbits of particles in such a potential are closed, which in turn is

related to the conservation of a vector quantity called the Runge-Lenz vector, which classically is given by

$$\mathbf{n} = \frac{1}{m}\mathbf{p} \times \mathbf{l} - \frac{e^2}{r}\mathbf{r}, \tag{27}$$

or quantum mechanically by the operator

$$\mathbf{N} = \frac{1}{2m}[\mathbf{P} \times \mathbf{L} - \mathbf{L} \times \mathbf{P}] - \frac{e^2}{r}\mathbf{r}. \tag{28}$$

You can read more about the links between conservation, symmetry, and degeneracy in the more advanced text book "Principles of Quantum Mechanics, 2nd Edition" by R. Shankar.